

Liquid-Vapor Transition and Critical Behavior of The Ultrasoft Restricted Primitive Model of Polyelectrolytes : a Monte Carlo Study

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Abstract

We present a Monte-Carlo study of the liquid-vapor transition and the critical behavior of a model of polyelectrolytes with soft gaussian charge distributions introduced recently by Coslovich, Hansen, and Kahl [J. Chem. Phys. **134**, 244514 (2011)]. A finite size study involving four different volumes in the grand canonical ensemble yields a precise determination of the critical temperature, chemical potential, and density of the model. Attempts to determine the nature of the criticality and to obtain reliable values for the critical exponents are not conclusive.

Keywords: Coulomb criticality; Monte Carlo simulations; Grand canonical ensemble; Critical phenomena; Finite size effects

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I. INTRODUCTION

After nearly twenty years of endeavors to elucidate the nature of the critical behavior of classical Coulombic liquids, no firm conclusion concerning this issue has yet been provided by theory, experiment and computer simulation. The long range of Coulomb potential would suggest classical mean field criticality, while the Debye-Hückel screening, yielding short range effective interactions, would rather suggest an Ising-like critical behavior [1–6]. The more recent contributions of the Orsay group on the type of Coulomb criticality is a finite size scaling (FSS) analysis of grand canonical Monte Carlo simulations of the liquid-vapor transition of the three dimensional (3D) restricted primitive model of electrolytes (RPM), *i.e.* a fluid of charged hard spheres of opposite charges and equal diameters [7]. The conclusions of this analysis unambiguously discard mean field behavior and rather suggest that the 3D-RPM belongs to the universality class of the 3D-Ising model. After a lot of controversy, most authors who contributed to this issue seem now in favor of an Ising-like criticality [8, 9].

The numerical simulations of the RPM in the critical region are notably plagued by many numerical difficulties : the usual critical slowing down and, more specifically, the long range of the Coulombic interaction and the unusually low values (in natural reduced units) of the critical temperature ($T_c^* = 0.04917(2)$) and the density ($\rho_c^* = 0.080(5)$). Therefore the new model of polyelectrolytes introduced in Ref. [10–12] is welcome and could well provide a new interesting toy model for studying Coulomb criticality, irrespective of its validity to reproduce the physics of polyelectrolytes. The ultrasoft restricted primitive model (URPM) of polyionic solutions is a mixture of positive and negative extended charge distributions, hence the alternative denomination of "fuzzy polyelectrolytes". To make things easier all polyions share the same shape factor $\tau(\mathbf{r})$. Of course the net global charges of cations and anions are of opposite values $\pm Q$. The system is H-stable in the sense of Fisher and Ruelle [10, 13, 14] and therefore admits a well behaved thermodynamic limit. The key point is that additional short range interactions such hard cores are not required to ensure thermodynamic stability. Of course both the RPM and the URPM are expected to belong to the same universality class. The URPM is conceptually the simplest model of Coulombic fluid with -possibly- a critical point and it thus deserves the closest attention.

The authors of Ref. [10–12] made the choice of a gaussian distribution for $\tau(\mathbf{r})$ which yields

simple analytical expressions for the ionic interactions. Their Monte Carlo and Molecular Dynamics simulations of the gaussian URPM in the fluid phase reveal the existence of a liquid-vapor coexistence curve. It is noteworthy that the many theories examined in Refs [12, 21–23] seem to be unable to reproduce the simulation results in the vicinity of the critical point.

Here we report new MC simulations in the critical region aimed at a more precise location of the critical point and an attempt to obtain the critical exponents. These simulations were performed in the grand-canonical (GC) ensemble using a cubic simulation cell with periodic boundary conditions together with Ewald potentials [15]. We considered 4 different volumes $V = L^3$ and, for each volume, we made use of histogram reweighting to determine the histograms $p_L(\rho, u)$ (ρ numerical density, u energy per unit volume) in a domain of temperatures and chemical potentials close to that of the critical point [16].

Our paper is organized as follows: in section II we explicit the model and we then give details on our simulations in section III. The results are discussed in section IV and conclusions are drawn in section V.

II. THE MODEL

The URPM is an equimolar mixture of $N_+ = N/2$ cations of charge $+Q$ and $N_- = N/2$ anions of charge $-Q$ in a volume V . Cations and anions bear an extended charge distribution $\pm Q\tau(\mathbf{r})$ where the distribution $\tau(\mathbf{r})$, normalized to unity, is supposed to be the same for all species of polyions and given by a Gaussian law :

$$\tau(\mathbf{r}) = \left(\frac{1}{2\pi\bar{\sigma}^2} \right)^{3/2} \exp(-\mathbf{r}^2/(2\bar{\sigma}^2)) , \quad (1)$$

where $\bar{\sigma} = \sigma/2$ denotes the radius of the polyion, σ its diameter. The polyions interact only through electrostatic interactions. The pair interaction between an α and a β polyon ($\alpha, \beta = +$ or $-$) is given by [11]

$$w_{\alpha\beta}(r) = \frac{Q_\alpha Q_\beta}{r} \operatorname{erf}(r/2\bar{\sigma}) , \quad (2)$$

and, in Fourier space

$$\tilde{w}_{\alpha\beta}(k) = \frac{4\pi Q_\alpha Q_\beta}{k^2} \exp(-k^2\bar{\sigma}^2) . \quad (3)$$

The polyions interact only through the electrostatic interactions (2) and no additional soft or hard repulsive interaction is required. In particular, at low temperatures, cations and anions can interpenetrate and form pairs of polarizable dipoles. We thus expect the system to behave as a quasi ideal gas ($\beta p/\rho = 1/2$, p pressure) at low temperatures. In the case of the usual RPM this possibility is thwarted by the presence of hard cores. However, it is easy to show that the configurational energy of the URPM is nevertheless bounded by below by a finite extensive quantity $-N_+w_{++}(0) - N_-w_{--}(0)$ (with finite self-energies $u_0 \equiv w_{++}(0) = w_{--}(0) = Q^2/(\sqrt{\pi}\sigma)$). Therefore the system is H-stable in the sense of Fisher and Ruelle which ensures the existence of the thermodynamic limit (TL) [13, 14]. In particular the grand partition function converges and can be computed without altering its TL value by enforcing the charge neutrality of all configurations, *i.e.* imposing $N_+ = N_-$. Indeed a theorem by Lieb and Lebowitz ensures that the TL of the unconstrained and neutral systems are the same in the GC ensemble [17].

To make some contact with the literature on the RPM it seemed preferable to us to chose σ as the unit of length rather than $\bar{\sigma}$ or $\sqrt{2}\bar{\sigma}$ as in Refs. [10–12]. Henceforth the reduced density of the system is denoted by $\rho^* = N/V^*$ with a reduced volume $V^* = V/\sigma^3$. In the same vein we define the reduced temperature as $T^* = k_B T/u_0$ (temperature in Kelvin, k_B Boltzmann constant) and its dimensionless inverse $\beta = 1/T^*$ (our unit of energy is thus the same as that of Refs. [10–12]).

III. MONTE CARLO SIMULATION

A. Ewald sums

We considered a cubic simulation cell of side $L^* = L/\sigma$ with periodic boundary conditions and we made use of Ewald potentials to take into account the long range of Coulomb interactions. The configurational energy U of the URPM is made of three contributions U_r , U_k , and U_s of which the two first are series of functions, respectively defined in direct and Fourier space, both with good convergence properties, see *e.g.* [15], and U_s is a self-energy term. U reads as [11]

TABLE I: The table displays, for each reduced volume V^* , the range of temperatures T^* , the total number n_T of distinct thermodynamic states (μ_i, β_i) , the total number n_c of selected configurations (spaced by 1500 trial moves), the apparent critical temperatures $T_c^*(L)$, chemical potentials $\mu_c^*(L)$, and densities $\rho_c^*(L)$ as they are defined in Section IV. Numbers in brackets denote the error on the last digit.

V^*	T^*	n_T	n_c	$T_c^*(L)$	$\mu_c^*(L)$	$\rho_c^*(L)$
500	$0.010 \leq T^* \leq 0.019$	129	$5.3 \cdot 10^8$	0.0181(1)	-0.192104(1)	0.21(1)
1000	$0.011 \leq T^* \leq 0.019$	122	$5.7 \cdot 10^8$	0.0162(1)	-0.189923(1)	0.225(5)
2000	$0.012 \leq T^* \leq 0.019$	181	$1.1 \cdot 10^9$	0.0150(1)	-0.188656(1)	0.23(1)
4000	$0.013 \leq T^* \leq 0.018$	59	$1.8 \cdot 10^9$	0.0142(1)	-0.187934(1)	0.27(1)

$$U = U_r + U_s - U_s \quad (4a)$$

$$U_r = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{r_{ij}} \left(\text{erf}(r_{ij}/\sigma) - \text{erf}(r_{ij}/(\sqrt{2}\tilde{\sigma})) \right), \quad (4b)$$

$$U_k = \frac{1}{2V} \sum_{\mathbf{k} \neq \mathbf{0}} \frac{4\pi}{k^2} \exp(-\mathbf{k}^2 \tilde{\sigma}^2/2) |\tilde{\rho}_{\mathbf{k}}|^2 \quad (4c)$$

$$U_s = \frac{NQ^2}{\sqrt{2\pi}\tilde{\sigma}} \quad (4d)$$

In Eqs. (4) $\tilde{\sigma} = \sqrt{\sigma'^2 + \bar{\sigma}^2}$ is related to the control parameter σ' of the Ewald method. The pair distances r_{ij} in (4b) are computed with the minimum image convention and the function $\text{erf}(r_{ij})$ is set to zero for $r_{ij} > L/2$. In Eq. (4c) $\mathbf{k} = 2\pi\mathbf{n}/L$, where $\mathbf{n} \in \mathbf{Z}^3$ is a vector with 3 integer components. In practice, only the vectors with a modulus $||\mathbf{n}|| \leq 7$ are considered in the sum in the r.h.s. of (4c). Finally $\tilde{\rho}_{\mathbf{k}} = \sum_{i=1}^N Q_i \exp(i\mathbf{k} \cdot \mathbf{r}_i)$ denotes the Fourier transform of the microscopic charge density. In our simulations, in reduced units, $\sigma' = \sigma = 1$ and thus $\tilde{\sigma} = \sqrt{5}/2$.

B. Grand-Canonical ensemble and Histogram Reweighting

We performed MC simulations in the GC ensemble which is well suited for the simulation of multiphase systems [15]. In the GC ensemble the volume V , the inverse temperature β and the chemical potential μ are fixed. We considered 4 different reduced volumes $V^* =$

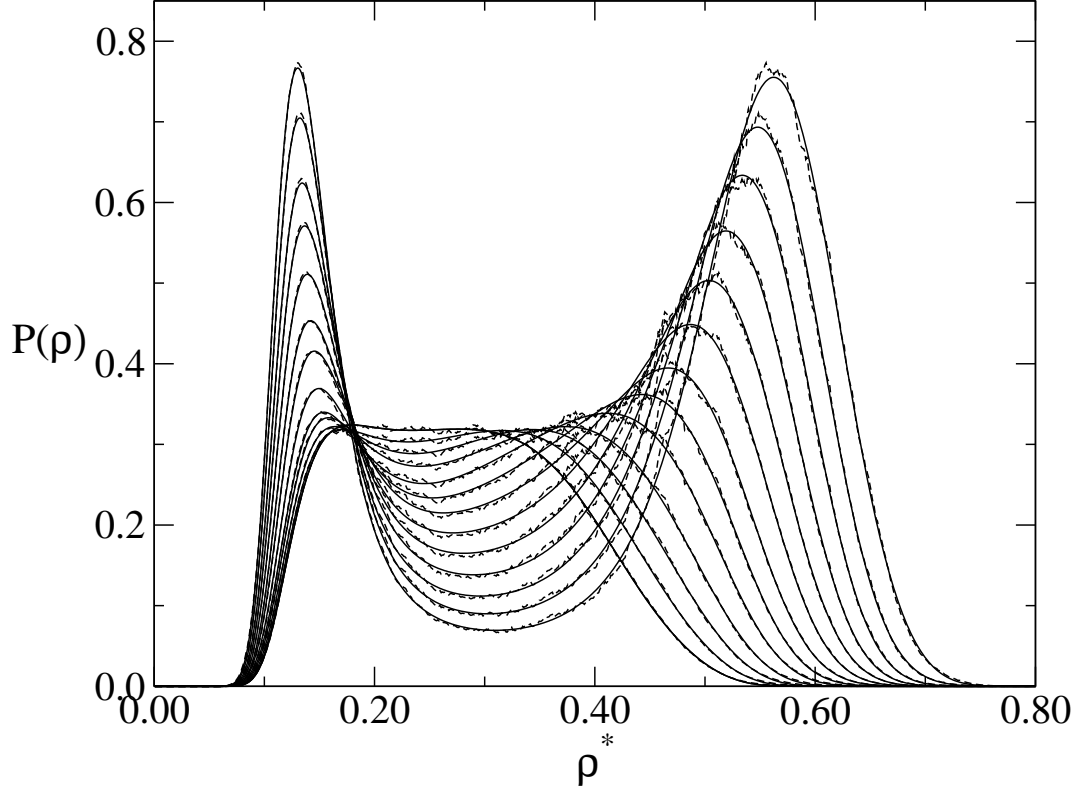


FIG. 1: Density histograms at coexistence for a reduced volume $V^* = 2000$ and reduced temperatures in the range $0.0126 < T^* < T^* = 0.0150$ by increments of $\delta T^* = 0.0002$. Dashed lines: MC data after reweighting, solid lines: fits.

500, 1000, 2000 and 4000 in order to study and exploit FSS effects. This should be compared with the simulations of Ref. [10], also performed in the grand canonical ensemble for volumes of $V^* = 282$ and $V^* = 1123$ in our units. It was not necessary to use the biased MC schemes usually considered for the RPM (see e. g. Ref. [7, 9]) and we thus made use of the standard Metropolis algorithm [15]. In addition to the trial displacements of individual polyions we only considered trial insertions or deletions of a single pair of an anion plus a cation in order to preserve the overall charge neutrality $N_+ = N_-$.

During the simulation runs we recorded, at fixed μ , β , and V , the joint distribution $p_L(\rho, u)$ of the numerical density ρ and energy density $u = U/V$ which is the basic ingredient of our analysis of the critical properties. For each volume and temperature typically a dozen of chemical potentials was considered in order to span a wide domain of liquid and gaseous states near criticality. For each volume we thus considered more than a hundred of thermodynamic states. The acceptance rate for insertion or deletion of a pair of anion-cation

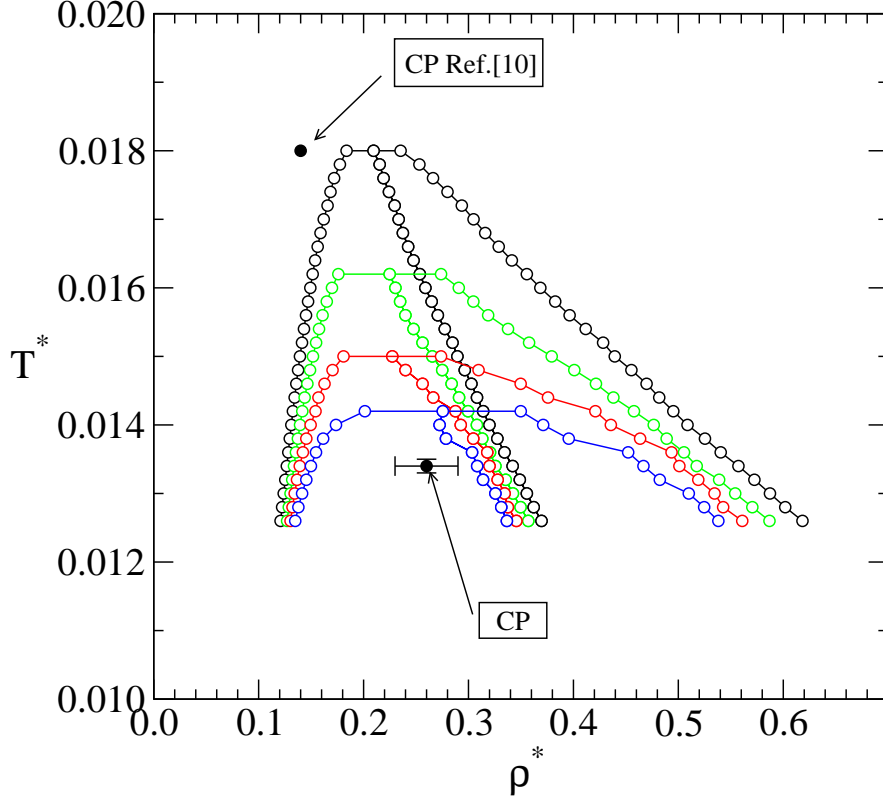


FIG. 2: Coexistence curves $\rho_g(T^*)$ and $\rho_l(T^*)$ for the volumes $V^* = 500$ (black), $V^* = 1000$ (green), $V^* = 2000$ (red), and $V^* = 4000$ (blue). We also display the curves $(\rho_g(T^*) + \rho_l(T^*))/2$ which roughly satisfied the law of rectilinear diameters. Solid circles : estimates for the critical points.

was $\sim 10^{-4}$ and ~ 0.3 for the displacements. The total amount of generated configurations was about 10^{12} of which we kept only one out of 1500 to build the histograms. Use of multi-histogram reweighting was made to infer the joint distribution $p_L(\rho, u)$ for a quite wide domain in the (β, μ) plane, close to the critical point (β_c, μ_c) , from the ones obtained for each individual state (β_i, μ_i) considered in the MC runs [16]. Table I summarizes some of the technical characteristics of our simulations.

IV. RESULTS

Our simulations confirm the existence of the liquid-vapor transition of the URPM discovered in refs [10, 11]. For each considered volume V and for each temperature smaller than some effective $T_c(L)$, we obtained a bunch of bimodal density histograms $p_L(\rho)$ for chemical

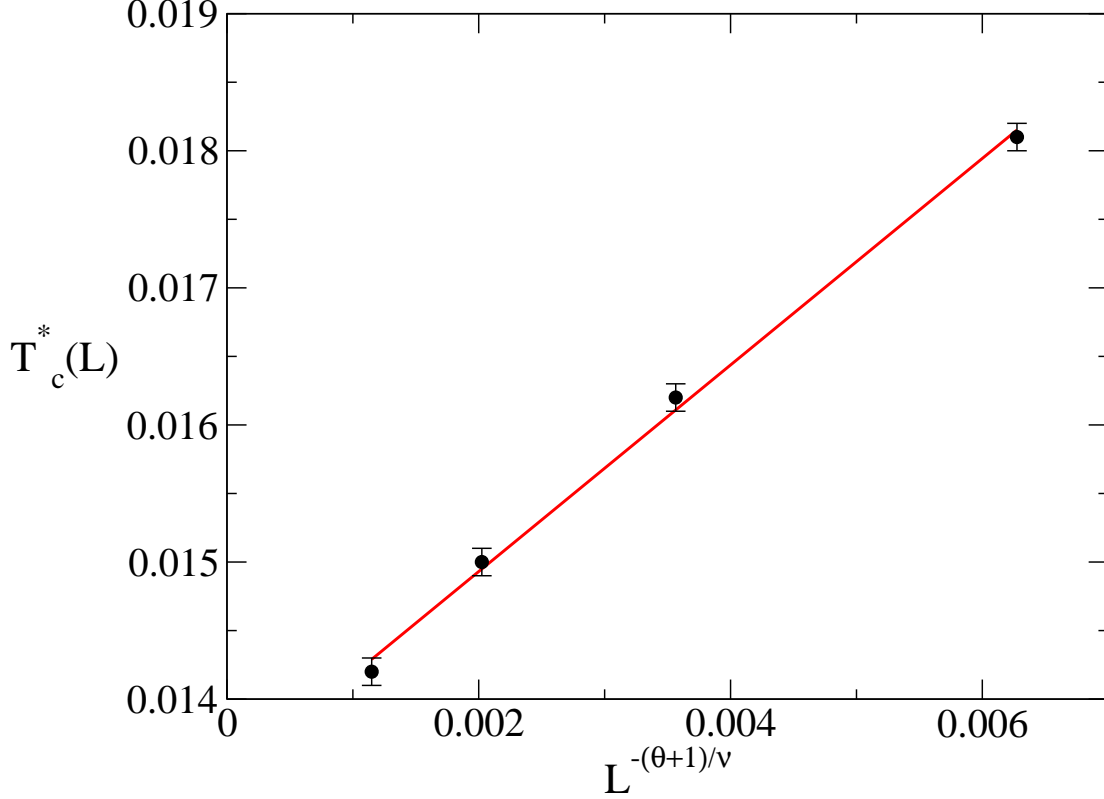


FIG. 3: Apparent critical temperature $T_c^*(L)$, as defined in the text, vs $L^{-(1+\theta)/\nu}$, where the exponents θ and ν are those of the universality class of the 3D-Ising model. The $T_c^*(L)$ are 0.0181, 0.0162, 0.0150, and 0.0142 for $V^* = 500$, $V^* = 1000$, $V^* = 2000$, and $V^* = 4000$ respectively. Red solid line : linear regression of the MC data $y = 0.013424 + 0.75334 * x$, giving the infinite volume limit $T_c^*(\infty) = 0.0134(1)$.

potentials μ close to the chemical potential $\mu_{\text{coex}}(T)$ at coexistence. Here $\mu_{\text{coex}}(T)$ is defined as the one that ensures that the two peaks of the histogram have the same height. It then follows that the pressures of the two coexisting phases are equal. Figure (1) displays some histograms $p_L(\rho)$ at coexistence for $T < T_c(L)$ and the reduced volume $V^* = 2000$.

Once $\mu_{\text{coex}}(T)$ determined, $p_L(\rho)$ is conveniently fitted by the exponential of a polynomial and the densities $\rho_l(T)$ and $\rho_g(T)$ of the liquid and the gas are obtained as the zeros of the derivative of this polynomial. At some temperature $T_c(L)$ only one zero survives, giving an estimate of an apparent critical temperature $T_c(L)$. The coexistence curves for the different volumes are given in Figure (2). Note that the law of rectilinear diameters is only but roughly satisfied and the critical density $\rho_c(L)$ is obtained from an extrapolation.

As apparent on Figure (2) the curves depend strongly on the system size L . Although

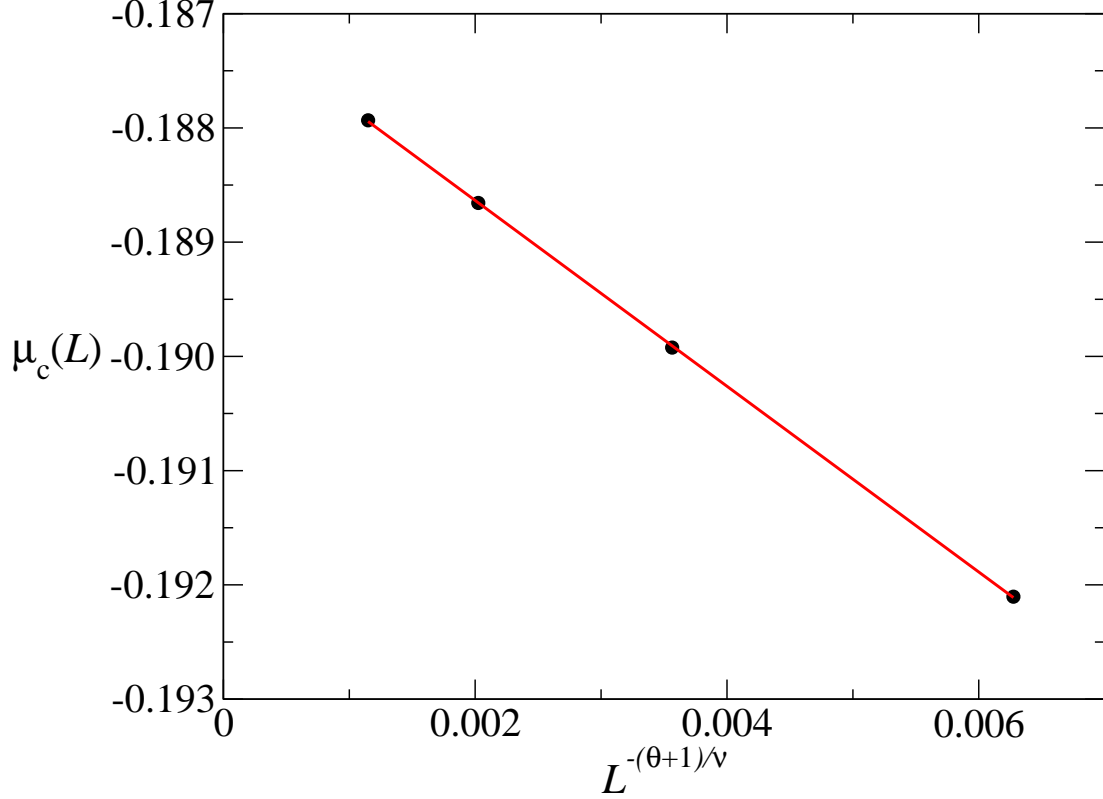


FIG. 4: Apparent critical chemical potential $\mu_c(L)$, as defined in the text, vs $L^{-(1+\theta)/\nu}$, where the exponents θ and ν are those of the universality class of the 3D-Ising model. Red solid line : linear regression $y = -0.18701 - 0.81317 * x$. The error bars on $\mu_c(L)$ are smaller than the sizes of the symbols

such a huge dependency seems to imply that the considered volumes are not large enough to achieve the critical scaling regime, the $T_c(L)$ values have been used to obtain an estimate of $T_c(\infty)$ by supposing $T_c(L)$ linearly dependent on L^{-a} as in the scaling limit. It turns out that the a value is very close from the value expected for an Ising-like criticality, *i.e.* $a \simeq (\theta + 1)/\nu$ where ν and θ are respectively the correlation length exponent and correction to scaling Wegner exponent [18–20]. The Ising values of ν and θ are 0.63 and 0.53 and give $a \sim 2.44$. The curve of $T_c(L)$ versus $L^{-(\theta+1)/\nu}$ is displayed in Figure (3) and Table I. Indeed a typical linear behavior is obtained leading to an extrapolated critical temperature $T_c^* \equiv T_c^*(\infty) = 0.0134 \pm 0.0001$. Note that, by contrast, making the hypothesis of a mean field criticality $T_c(L)$ would rather scale as L^{-3} (no hyperscaling!) [29] which, however, is not the behavior that we observed. This estimate differs from that given in Ref. [10], *i.e.* $T_c^* = 0.018$ which was obtained for smaller system sizes (*cf.* above) and without finite scaling

size analysis.

It turns out that the chemical potential also scales with system size as $\mu_c(L) \sim L^{-(\theta+1)/\nu}$ yielding $\mu_c = -0.18701 \pm 0.00001$, with an excellent precision, see Figure (4) and Table I. The critical density in the TL is obtained with much less precision and one finds $\rho_c^* = 0.26 \pm 0.03$.

In addition to this heuristic and approximate determination of the critical point in the thermodynamic limit, we have attempted quantitative FSS analyses of our URPM simulation data by using several theoretical frameworks proposed to determine the critical properties. These analyses confirm that these data are not in the scaling regime.

- (i) Field mixing.

Following the seminal work of Bruce and Wilding [18, 19] many simulation results of off-lattice critical fluids have been analyzed along the lines of the revised scaling theory of Rehr and Mermin [24]. In this (approximate) analysis one establishes a mapping between the fluid and the 3D-Ising model which restores the Z_2 symmetry. The two relevant scaling operators \mathcal{M} (magnetization) and \mathcal{E} (magnetic energy) of the associated Ising model are supposed to be linear combinations of the fluid variables ρ and u near criticality. For a given volume V and at a given apparent critical temperature the histogram $p(\mathcal{M})$ of the order parameter should collapse on a universal function, typical of the 3D Ising universality class $p^*(\mathcal{M})$ known from lattice spin simulations [25]. In ref. [7] the MC data on the RPM have been successfully analyzed within this framework. Here, for the URPM, and quite unexpectedly, it was impossible to find reasonable field mixing parameters in order to obtain a collapse of $p(\mathcal{M})$ onto the universal $p^*(\mathcal{M})$. Clearly, even the largest considered volume $V^* = 4000$ seems far from the scaling regime.

- (ii) The locus $\chi_{N^3} = 0$.

This scheme was proposed in Ref. [26]: one studies several well chosen density and/or energy fluctuations $\chi_{N^k U^m} = \langle (N - \langle N \rangle)^k (U - \langle U \rangle)^m \rangle$ along the locus $\chi_{N^3} = 0$ of the phase diagram (to which the apparent critical point at volume V necessarily belongs). This is an alternative way used to restore the Z_2 symmetry in the model. Some fluctuations exhibit extrema along this locus, the position and the height of which should scale smoothly with system size. Our data reveal a non monotonous behavior with L which suggests that the scaling regime has not yet been reached.

- (iii) The Q-locus.

We follow here a suggestion by Kim and Fisher [27] very similar to the previous item. Binder's cumulant [28] $Q_L = \chi_{N^2}^2 / \chi_{N^4}$ is computed along the Q-locus, *i.e.* the locus of the maxima of Q_L at a given T in the T, μ plane. Scaling laws reminiscent to that of the Ising model then should apply to Q_L along the Q-locus. This analysis turned out not to be possible for the URPM mainly because the intersections of the various curves $Q_L(T)$ do not follow a monotonous behavior.

These failures strongly suggest that our simulations are far from the scaling regime and that the usual FSS analysis is not relevant. It should be mentioned that the range of the apparent critical temperatures spreads from $T_c^*(L) = 0.0181 \sim 1.35 \times T_c^*(\infty)$ for $V = 500^*$ to $T_c^*(L) = 0.0142 \sim 1.059 \times T_c^*(\infty)$ for $V = 4000^*$, with an infinite volume extrapolation of $T_c^*(\infty) = 0.0134$. These ranges of variations are huge when compared to those considered in the simulation of the RPM in Ref. [7] where all the apparent critical temperatures $T_c(L)$ do not differ from $T_c(\infty)$ by more than 0.35%. Our simulations of the URPM involved too small samples and the scaling limit was probably not yet obtained.

V. CONCLUSION

We have performed MC simulations of the ultrasoft restricted primitive model of polyelectrolytes in the grand canonical ensemble. Our simulations confirm the existence of a liquid-vapor transition and allow us to give the following estimations for its critical point

- $T_c^* = 0.0134(1)$
- $\mu_c = -0.18701(1)$
- $\rho_c^* = 0.26(3)$

These estimates were obtained by a partial FSS analysis assuming a 3D-Ising like criticality. A full FSS analysis of the MC data was however not possible since the scaling limit was not reached, even in the case of the largest volume $V^* = 4000$ considered in the study. A complete FSS analysis would thus require to consider much larger volumes than $V^* = 4000$. The high value of the critical density, *i.e.* $\rho_c^* = 0.26$ would imply the simulation of liquid phases involving several thousand of polyions which seems unrealistic.

As mentioned in the introduction further studies of Coulomb criticality are wanted in next future. We suggest to consider the model with hard cores (*i.e.* the RPM) rather than the URPM to endeavor such studies. The URPM remains however appealing to test analytical theories.

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